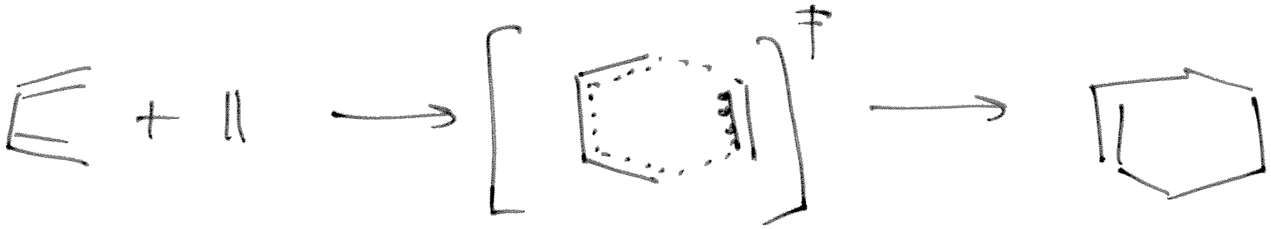
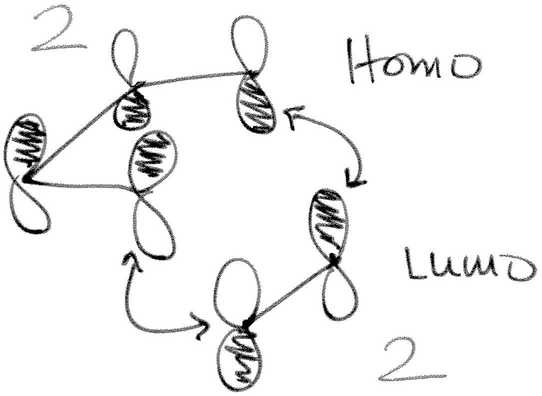
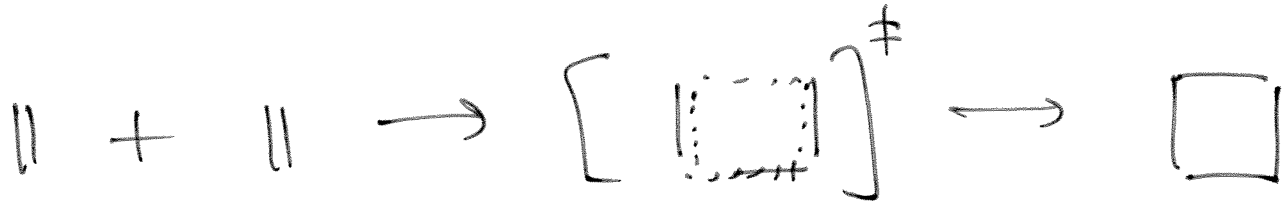
CHM 3120 MIDTERM ①

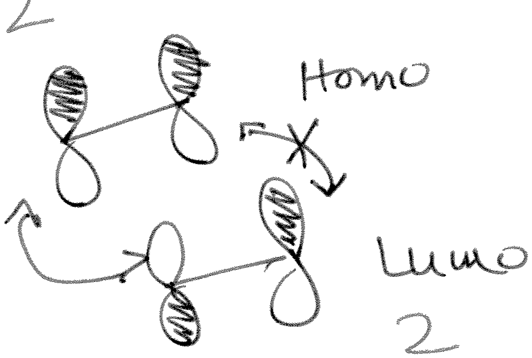
①





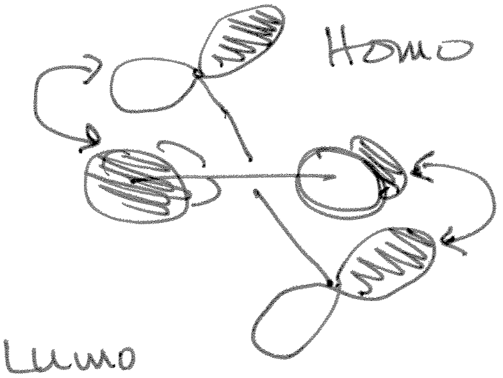
Overlapping orbitals of the same phase ∴ bond formation can occur.





One pair of overlapping orbitals are not in phase ∴ bond formation cannot occur.

This can happen at elevated T, but via a different TS structure:



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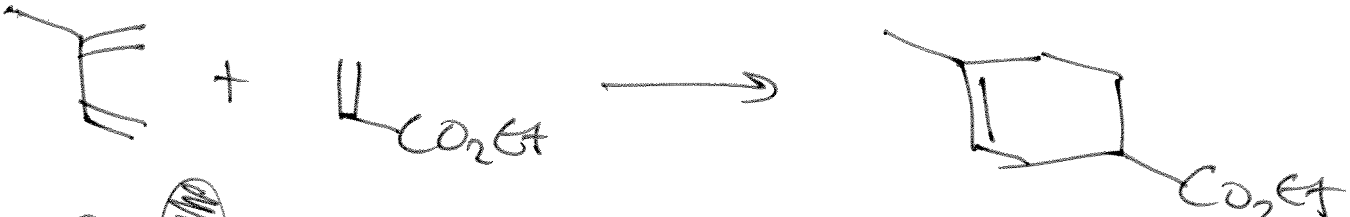

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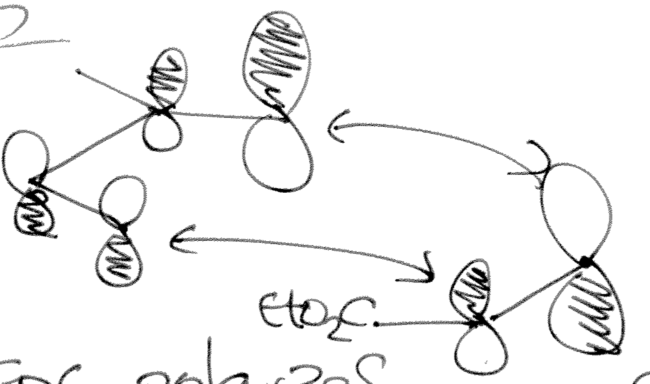

2

EDG polarizes HOMO

EWG polarizes LUMO

major product 2

due to MO polarization

Addition of $AlCl_3$ leads to increased polarization of the dienophile since it is Lewis Acidic and renders the dienophile more electrophilic, lowering the LUMO energy:

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This makes the coefficient (orbital contribution) on the β-carbon even larger in the LUMO, increasing the regioselectivity through its greater potential overlap w̄ the diene HOMO.

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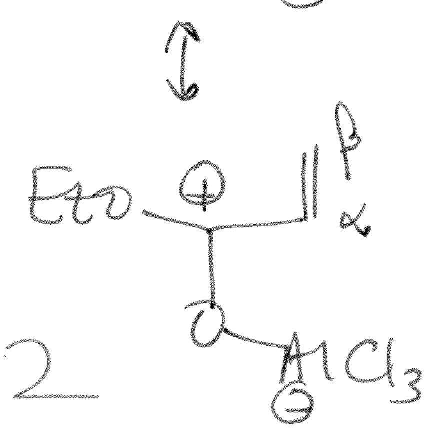

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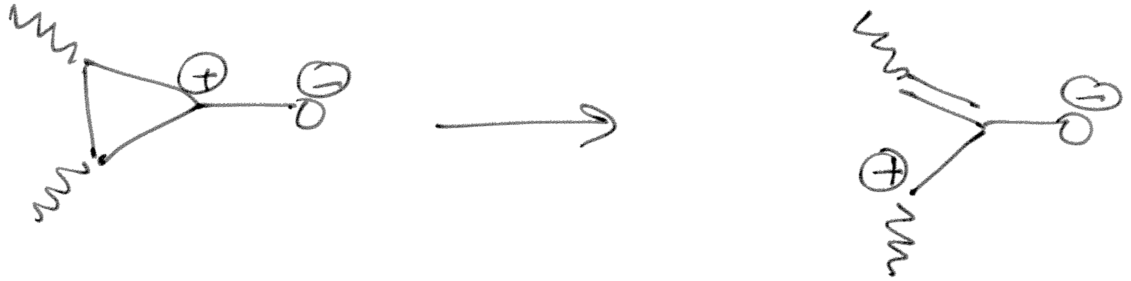
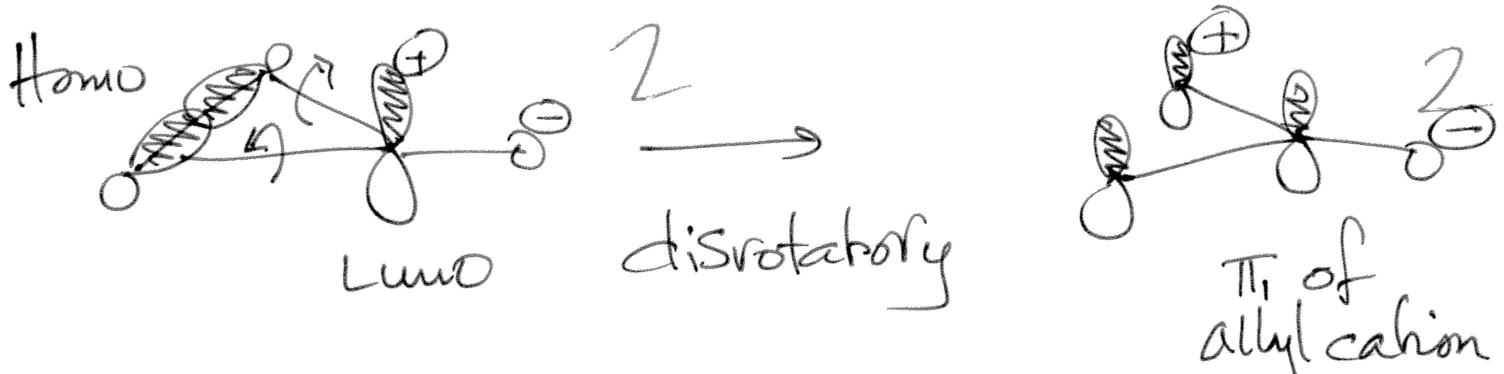
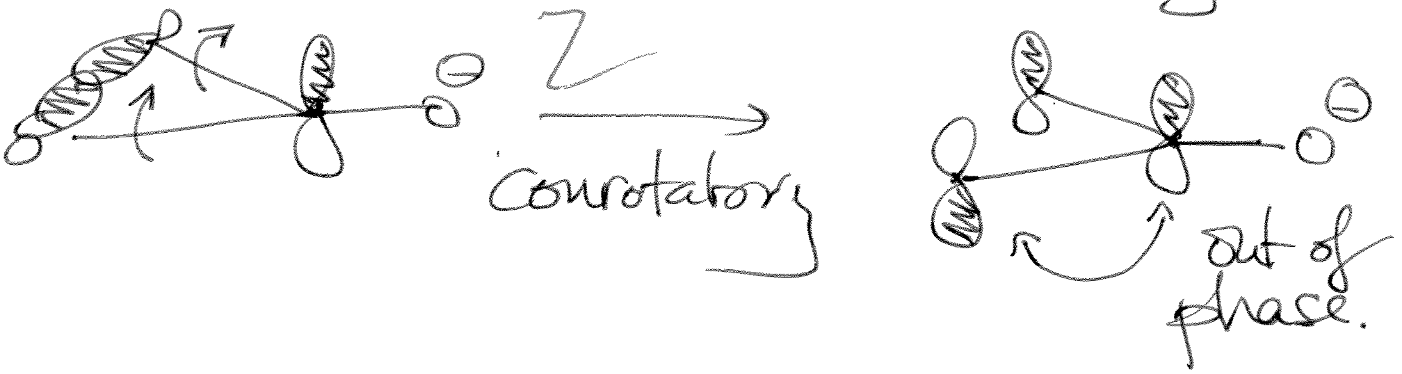
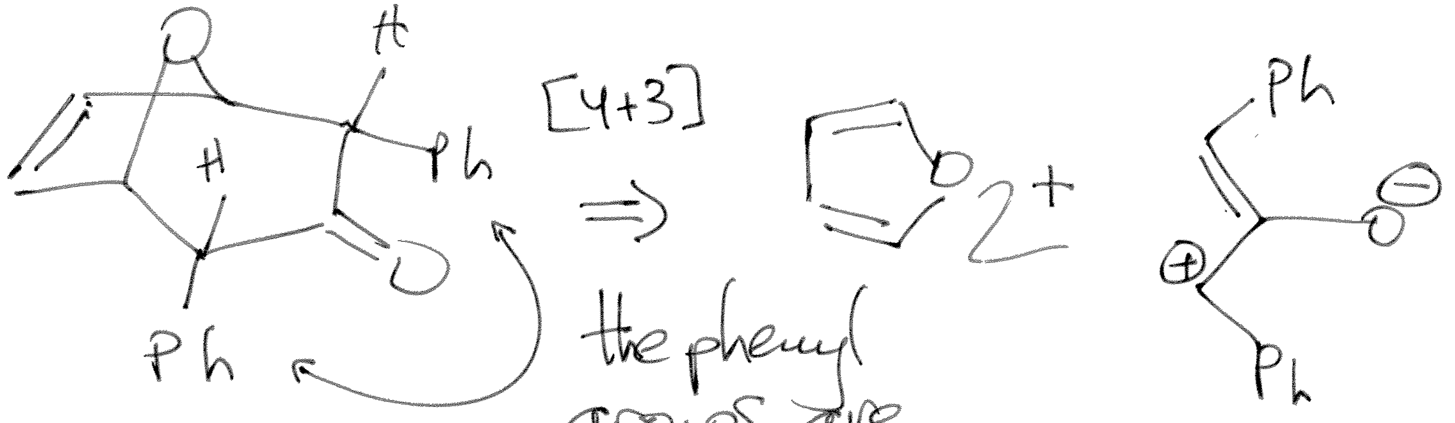
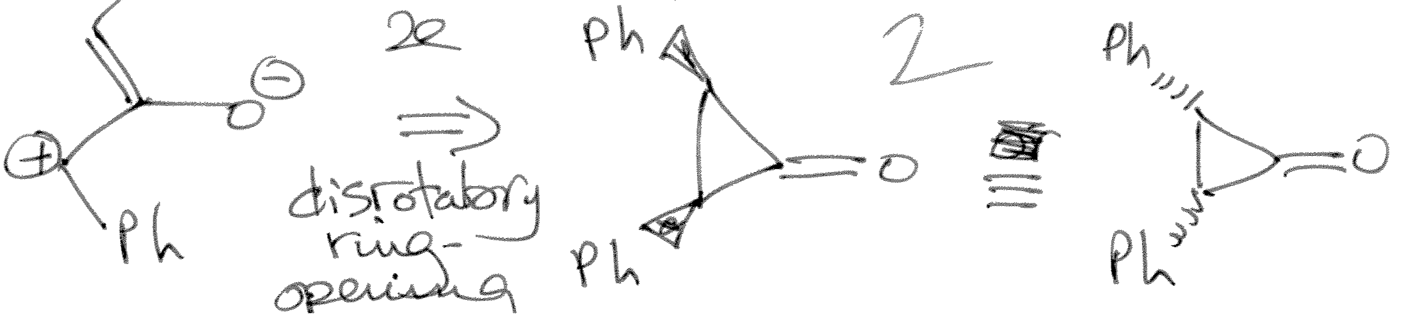








the phenyl groups are on the same face (syn/endo)



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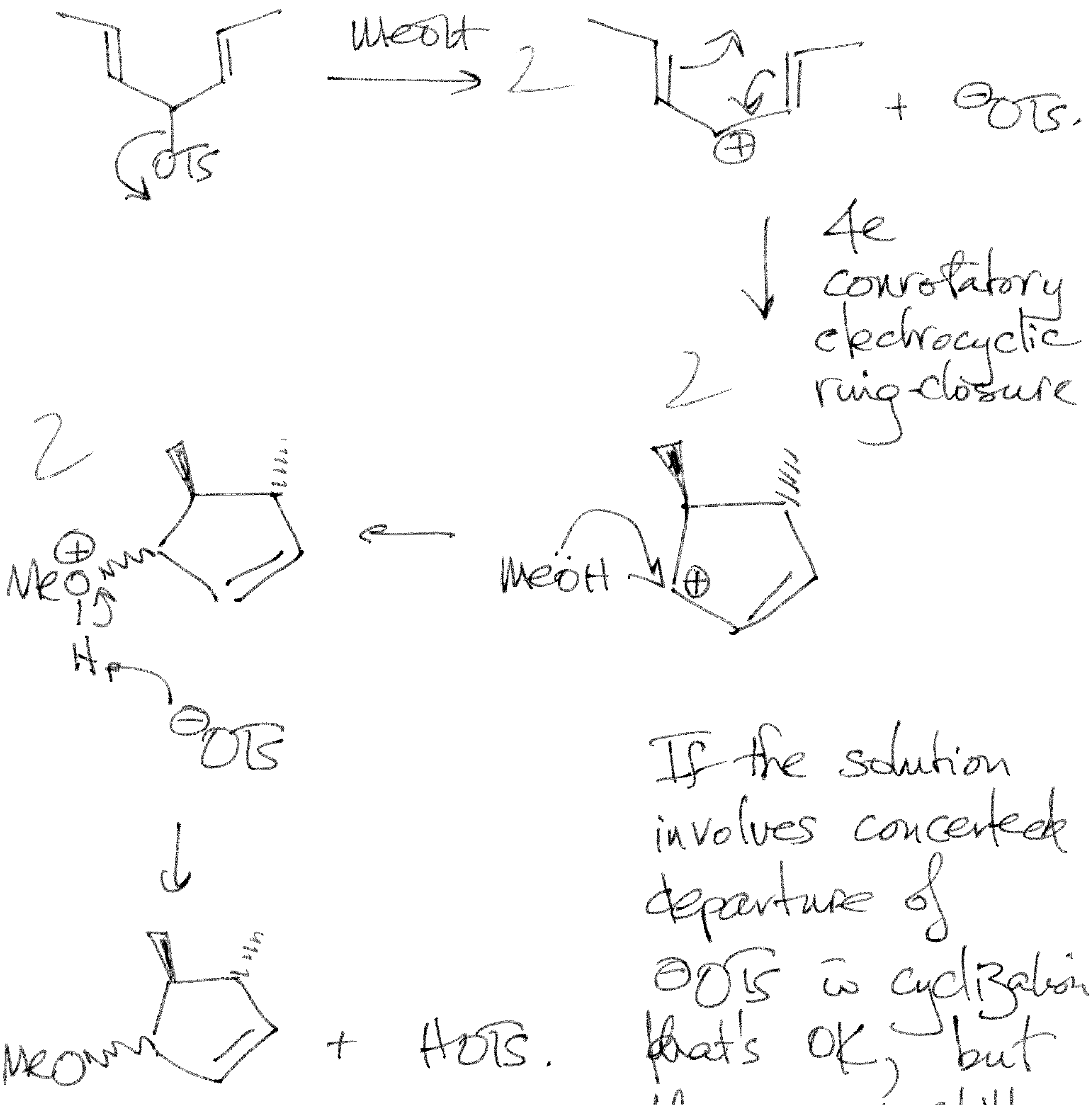
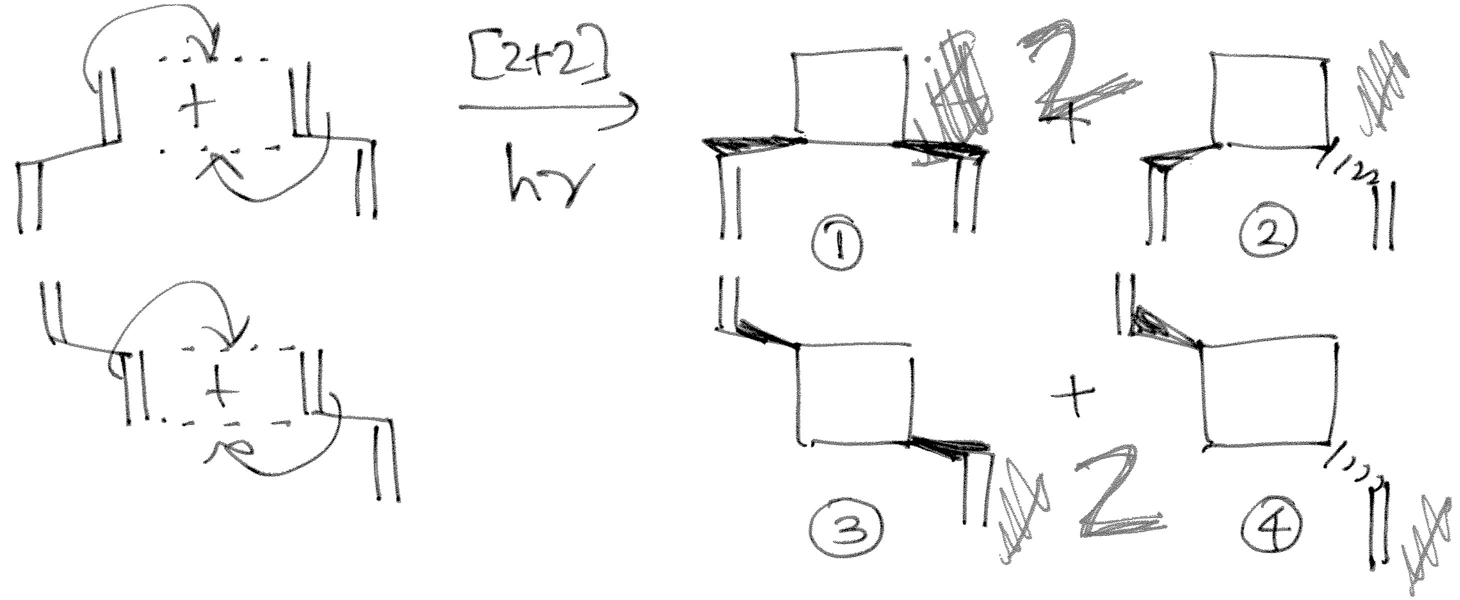


If the solution involves concerted departure of ⊖OTs in cyclization that's OK, but they must still identify that is a 4e conrotatory ring closure (now it involves the σ^*_{C-OTs})

5)



only isomer ① can undergo a [3,3] (Cope) sigmatropic rearrangement!

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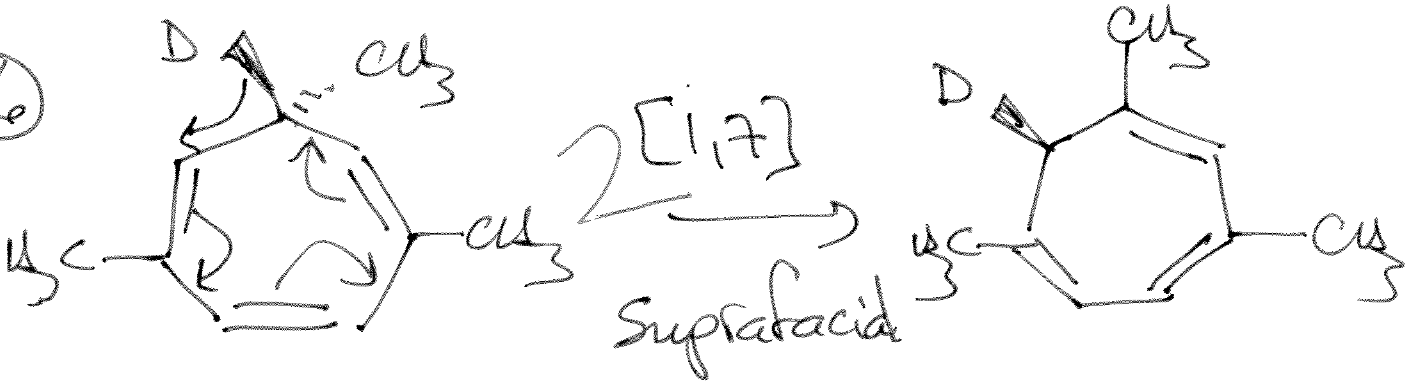
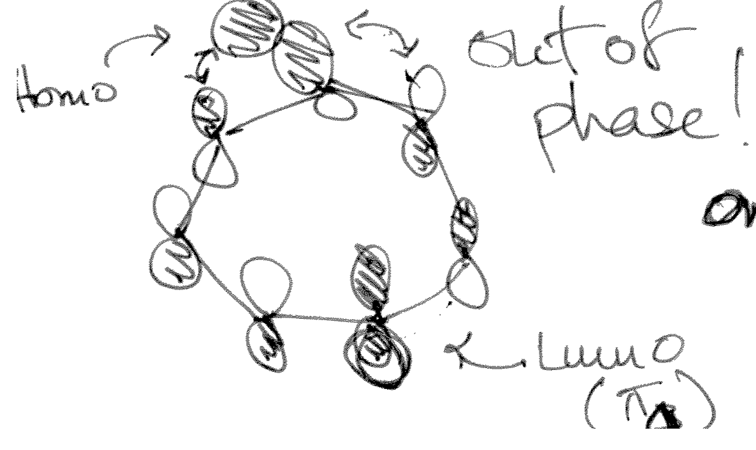
⑥



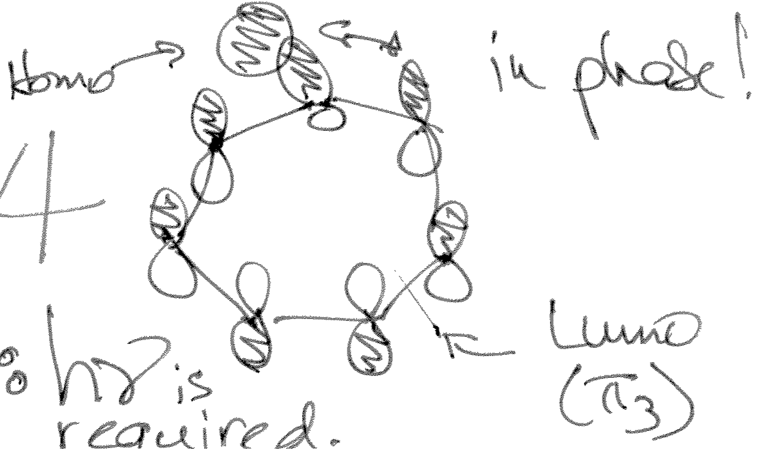
THERMAL CASE

PHOTOCHEMICAL CASE



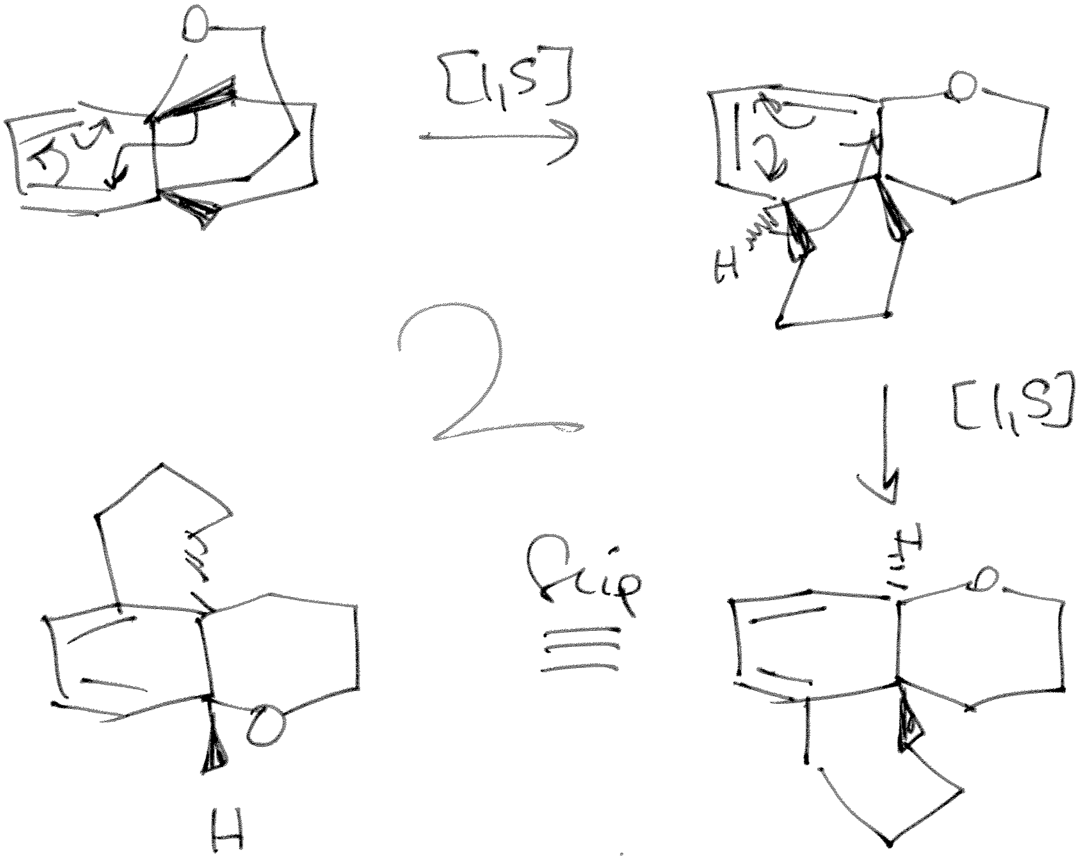
or

4



∴ hν is required.

BONUS.



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no part marks..